combination of the resultant CH_3 + LiH fragments to form CH_3LiH.

Conclusions

The $^2A_1$ ground state for CH_3LiH shows the species to be comprised of two weakly interacting parts, a methyl and lithium hydride. The higher excited ^2E states show greater interaction of these two parts but with less C–H bonding.

The pathway to insertion appears to be by an abstraction process of a hydrogen atom from CH_4 by a ^2P lithium atom followed by a relaxation of the two species with greater interaction, giving the $^2A_1$ CH_3LiH ground state.

Acknowledgment. The continuous financial support of the Natural Sciences and Engineering Research Council (NSERC) Strategic Grant Program of Canada is gratefully acknowledged.

Registry No. Li, 7439-93-2; CH_4, 74-82-8; CH_3LiH, 89922-18-9; CH_3, 2229-07-4; LiH, 7580-67-8.

Static and Dynamic Stability Criteria during Free Diffusion in a Ternary System

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The static and dynamic stability criteria valid for a two-layer ternary system are explained. Attention is concentrated on those systems for which the main diffusion terms greatly exceed the cross-diffusion terms. The results of experiments with the three systems water–KCl–glycine, water–urea–sucrose, and water–KCl–sucrose are shown to be in good agreement with the criterion for dynamic stability, rather than that for static stability as suggested by a previous author.

Introduction

Knowledge of the precise molecular diffusivity of a solute in water is required in many different disciplines. This requirement has been strengthened recently by the emergence of the new subject of double-diffusive convection, which studies the fluid motions driven by two or more components of different molecular diffusivities.[1-3] The measurement of the isothermal diffusion coefficients in a ternary system is frequently accomplished by setting up two solutions with a sharp horizontal interface between them in a diffusion cell. The experimentalist assumes that only molecular diffusion, and not fluid motion, broadens the concentration profiles in the neighborhood of the interface. He then calculates the diffusion coefficients from the measured concentration profiles as a function of time. It is clear that a necessary (but possibly not sufficient) condition for this procedure to be valid is that the density profile be statically stable; that is, light fluid always overlies fluid of greater density. Otherwise the density of the system is statically unstable and the upper solution would mix advectively with the lower.

The static stability of the density profile produced with time by the diffusion process was initially examined by Wendt.[4] In part of his paper Wendt considers the limit where the cross-term diffusion coefficients $(D_{12})_V$ and $(D_{21})_V$ can be neglected with respect to the main terms $(D_{11})_V$ and $(D_{22})_V$. With the notation that the faster diffusing solute, labeled 1, makes up the lower solution, while the slower diffusing solute, labeled 2, makes up the upper solution, the necessary condition for static stability is

$$R_\rho \equiv \Delta\rho_1/\Delta\rho_2 > \tau^{-1/2} \tag{1}$$

where

$$\tau \equiv (D_{22})_V/(D_{11})_V < 1 \tag{2}$$

and $\Delta\rho_1$ and $\Delta\rho_2$ are the initial density excesses due to solutes 1 and 2 in their respective layers. Wendt does not present any experimental evidence to support his conclusions.

Unaware of Wendt's work, Huppert and Manins[5] also investigated the necessary conditions for the stability of such a two-layer system. They argued that using principles developed in the theory of double-diffusive convection,[1,2] one could show the system to be dynamically unstable though remaining statically stable at all times. The dynamic instability is associated with the growth of random velocity fluctuations. The growth is caused by diffusion acting in two different ways. First, it leads to diffusive concentration profiles as sketched in Figure 1b, and then it allows these profiles to become dynamically unstable. This instability produces a structure termed double-diffusive fingers and is caused as follows. Consider a parcel of fluid near the interface displaced downward, as sketched in Figure 1d. The parcel takes on the surrounding concentration of the solute of higher diffusivity more rapidly than that of the solute of lower diffusivity. In this way the fluid parcel can become heavier than its surroundings and continue its

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(1) Turner, J. S. "Buoyancy Effects in Fluids"; Cambridge University Press: Cambridge, England, 1979.

(2) Huppert, H. E.; Turner, J. S. *J. Fluid Mech.* **1981**, *106*, 299–329.

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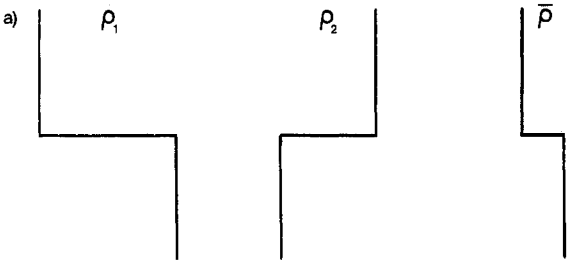
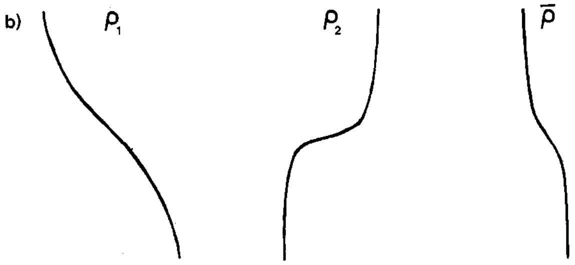
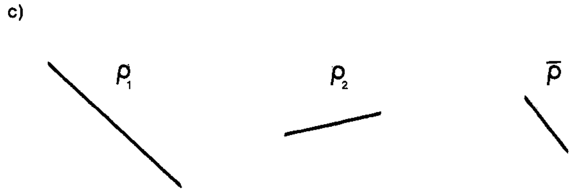


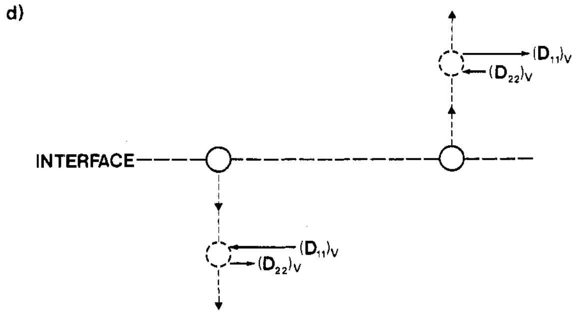
THE INITIAL DENSITY EXCESSES AND THE TOTAL DENSITY PROFILES



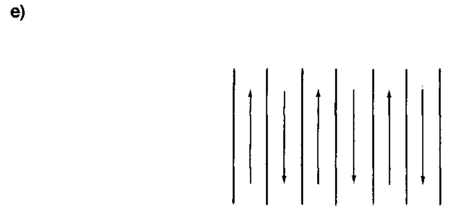
THE DENSITY EXCESSES AND TOTAL DENSITY PROFILES AFTER DIFFUSION HAS TAKEN PLACE



THE STRAIGHT LINE APPROXIMATIONS OF THE PROFILES IN b) AT THE LEVEL OF THE INTERFACE USED IN THE THEORETICAL ANALYSIS



SCHEMATIC REPRESENTATION OF THE DISPLACEMENT OF FLUID PARCELS SHOWING THE MAGNITUDE AND DIRECTION OF THE RESULTING DIFFUSION



THE STRUCTURE AND DIRECTION OF MOTION IN A WELL DEVELOPED SALT-FINGER FIELD

Figure 1. A pictorial representation of the development of a salt-finger field.

downward motion. A similar physical argument indicates that a parcel of fluid initially displaced upward continues to rise. In this way a structure of adjacent upward and downward moving fluid parcels can develop as sketched in Figure 1e. Photographs of this form of motion make up Figures 1 and 3 of Huppert and Turner.[2]

Using the above ideas, Huppert and Manins[5] calculate that a necessary condition for stability to such dynamic motions is that

$$R_\rho > \tau^{-3/2} \qquad (3)$$

A more rigorous theoretical treatment by Sartory[6] gives essentially the same result. It is unfortunately hidden somewhat in the paper, but it does appear in the sentence near the end of p 259 where it is stated that "$\mathcal{R}$ approaches 1 as T approaches infinity". $\mathcal{R} = 1$ can be written in the form of expression 3. On comparison with Wendt's static criterion (1), it is clear that the dynamical stability criterion (3) is stronger. Thus, if a stable system experiencing only diffusion is sought, (3) must be satisfied (which satisfies (1) automatically). In this case no small velocity fluctuations can disturb the stability of the system.

Huppert and Manins carried out some experimental tests of their derived criterion using the ternary systems water–salt–sucrose, water–salt–$MgSO_4$, and water–sucrose–$MgSO_4$. They obtained good agreement between their experimental results and theory. It could be objected, however, that the cross-terms for the systems used are unknown. These cross-terms could be large and agreement between theory and experiment fortuitous. Further, the water–salt–$MgSO_4$ system is actually a four-component system for diffusion. To determine which criterion is correct is clearly important. Indeed, it is interesting to note that at a recent international conference,[3] both the theoretical results (1) and (3) were presented by scientists unaware of each other's work.

The aim of the current experiments is to continue the discussion commenced at the conference and to explore ternary systems for which the cross-terms are known to be small. It is found that the results again agree well with the dynamical stability criterion (3) and show strong disagreement with the static stability criterion (1).

Based on the formulation of Huppert and Manins,[5] calculations have been made of the dynamical stability criterion including the effects of cross-terms.[7,8] In particular, criteria quite different from (3) can be valid when the cross-terms are large. These results await experimental confirmation.

Finally, it should be recalled that all the above applies only to the case where a fingering instability occurs due to the slower diffusing solute in the upper layer. No acceptable stability criterion has yet been obtained for the general case where the slower diffusing solute is in the lower layer.

Experiments

There are a large number of different ternary systems which could be used in the experiments. Some of these are tabulated in Table 4.4 of Cussler.[9] Since one aim of the experiments is to compare the results with associated theory, it is useful to choose ternary systems which conform to the theoretical assumptions as closely as possible. Thus, the diffusion coefficients should be known quantities over the concentration range employed in the experiments. In order to compare the results with the theory, systems with cross-term diffusion coefficients very much smaller than the main terms should be used. Ideally, the diffusion coefficients should be weak functions of the concentrations employed, since the theory assumes that they are constant. Finally, it saves considerable time if the density of each of the solutions can be obtained from refractive index measurements, since these can be quickly determined by using a temperature-compensating hand-held refractometer.

It seems impossible to find a ternary system which obeys all the above criteria. The three systems water–KCl–glycine, water–urea–sucrose, and water–KCl–sucrose were used, which at least have very small cross-terms in comparison with the main

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(8) McDougall, T. J. *J. Fluid Mech.* **1983**, *126*, 379–97.
(9) Cussler, E. L. "Multicomponent Diffusion"; Elsevier: Amsterdam, 1976.

diffusion terms.[10-12] The diffusivity in water of KCl is approximately 1.8 times greater than that of glycine, that of urea is approximately 2.3 times greater than that of sucrose, and that of KCl is approximately 3.5 times greater than that of sucrose. The values of these main terms and their ratios vary somewhat with concentration and the presence of the other component, but, as shall be detailed below, not sufficiently to cause any difficulty in the interpretations of the experimental results. Finally, tables[13] of the density of aqueous solutions of urea, sucrose, and KCl as a function of their refractive index are readily available. The density of the glycine solution used was determined by using a densitometer.

All the experiments were carried out in a Perspex container with internal dimensions 5.0 × 15.2 × 12.0 cm high at room temperature (ca. 20 °C). For the water–KCl–glycine experiments a standard glycine solution of density 1.0104 g cm^{-3} was prepared and KCl solutions of different densities were made up before each experiment as required. For the water–urea–sucrose and the water–KCl–sucrose experiments a standard solution of sucrose of density 1.0102 g cm^{-3} was used. Each experiment was carried out in the same manner as described by Huppert and Manins.[5] Approximately 400 cm^3 of the solution of higher diffusivity was poured into the container and a 1 cm thick foam strip presoaked in the solution of lower diffusivity was placed on the free surface. Approximately 400 cm^3 of the solution of lower diffusivity was then carefully added to form a two-layer system with a paper-thin interface.

The experiments were visualized by using the shadow-graph technique, which depends on the different refractive indices of the two solutions. Initially the interface, which is the region of largest refractive index and density change, was observed to broaden slowly by diffusion. In some experiments nothing other than this diffusive broadening was observed. In others, we saw a clear indication of a finger structure, which extended in time generally to a length of a few centimeters. In one or two experiments, which were carried out close to the limiting conditions, the fingers were very weak, but still definitely visible.

The values of τ were estimated for the three systems as follows. For the water–KCl–glycine system the four diffusion coefficients have been measured for six different concentration pairs.[10] In our experiments the concentrations at the center of the interface were approximately 0.25 mol L^{-1} for the KCl and 0.10 mol L^{-1} for the glycine. The concentrations closest to these at which the diffusion coefficients are known is 0.25 mol L^{-1} for each solution. At this concentration and at 25 °C

$$\begin{aligned}(D_{11})_V &= 1.800 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{12})_V &= -0.019 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{21})_V &= -0.018 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{22})_V &= 1.017 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ \tau &= 0.565\end{aligned} \tag{4}$$

We note that the magnitudes of the cross-terms are 50 times less than the smallest main term. While the individual diffusion coefficients vary slightly with concentration, the value of τ is remarkably uniform and varies by less than 2% over the six measurements.

For the water–urea–sucrose system the four diffusion coefficients have only been measured for urea and sucrose concentrations of 0.500 mol L^{-1} each.[11] The results at 25 °C are

$$\begin{aligned}(D_{11})_V &= 0.911 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{12})_V &= 0.06 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{21})_V &= 0.002 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{22})_V &= 0.391 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ \tau &= 0.429\end{aligned} \tag{5}$$

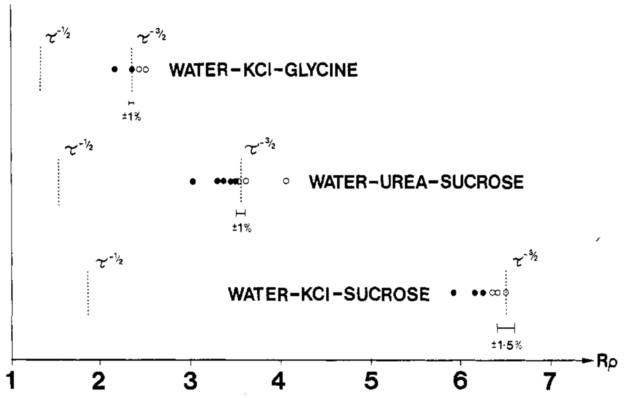

Figure 2. Experimental results for each of the three different systems as a function of R_ρ. ● indicates that fingering occurred at the interface and ○ that it did not. The vertical dotted lines are at $R_\rho = \tau^{-1/2}$ and $\tau^{-3/2}$, which are the theoretical relationships derived from a static and dynamic analysis, respectively. Errors in measuring R_ρ for each system are shown below the line $R_\rho = \tau^{-3/2}$.

The larger cross-term $(D_{12})_V$ is seen to be 15 times less than the main term $(D_{11})_V$.

For the water–KCl–sucrose system the four diffusion coefficients have been measured for four different concentration pairs.[12] In our experiments the density excesses at the center of the interface were approximately 0.032 g cm^{-3} for the KCl and 0.005 g cm^{-3} for the sucrose. The density excess closest to these for which the diffusion coefficients are tabulated is 0.03 g cm^{-3} for each solution. At this value, and at 25 °C

$$\begin{aligned}(D_{11})_V &= 1.739 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{12})_V &= 0.033 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{21})_V &= 0.024 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ (D_{22})_V &= 0.499 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}\\ \tau &= 0.287\end{aligned} \tag{6}$$

The cross-terms are 20 times less than the smallest main term.

Each of the diffusion coefficients at 25 °C can be linearly converted to those at any nearby temperature by using the Stokes–Einstein relationship. Thus the value of τ, since it is the ratio of two diffusion coefficients, is unaltered. We hence take at the temperature of the experiments

$$\begin{aligned}\tau &= 0.565 &&\text{(water–KCl–glycine)}\\ \tau &= 0.429 &&\text{(water–urea–sucrose)}\\ \tau &= 0.287 &&\text{(water–KCl–sucrose)}\end{aligned} \tag{7}$$

It is impossible to estimate strictly the errors in these values. The dominant contribution to the errors comes from the fact that the diffusion coefficients have been measured at concentrations different from those in the experiments. Perusal of the various measurements suggests that the error is likely to be less than 10%, but by how much less would be difficult to ascertain. We shall see, however, that the distinction between the two stability criteria is so large that the relatively small error in τ is unlikely to play a role in the interpretation of the experiments.

The results of the experiments are shown in Figure 2, wherein ● signifies that the fingers were observed along the interface and ○ that they were not. It is seen in the figure that there is a clear division between those values of R_ρ which support fingers and those which do not. Also marked on the figure are the estimated error bars of the measurements and the values of $R_\rho = \tau^{-3/2}$ and $\tau^{-1/2}$. These values correspond to the limiting conditions as outlined by the dynamic and static results (3) and (1), respectively. We see that these experimental results unambiguously support the dynamic theory of Huppert and Manins[5] rather than the static theory.

It would be interesting to carry out an analogous series of experiments with a ternary system for which the cross-terms

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(11) Ellerton, H. D.; Dunlop, P. J. *J. Phys. Chem.* **1967**, *71*, 1538–40.

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greatly exceed the main terms and then compare the results with the corresponding theory.[7,8]

Acknowledgment. It is a pleasure to thank D. G. Miller and H. J. V. Tyrrell for a series of stimulating discussions and correspondence. They brought to our attention Wendt's analysis and the data for the diffusion coefficients used in this paper. This research was partially supported by a grant from The Natural Environment Research Council.

Registry No. KCl, 7447-40-7; water, 7732-18-5; glycine, 56-40-6; sucrose, 57-50-1; urea, 57-13-6.

Molecular Statistical Thermodynamics of Model Micellar Aggregates

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A simple molecular model for micellar aggregates is studied by Monte Carlo computer experiments. The detailed structural and thermodynamic results implied by the model are presented and discussed. On the basis of these results, it is concluded that the repulsive forces which limit micellar growth to submacroscopic sizes must have a spatial range larger than, but roughly comparable to, the spatial extent of the micelles of most probable aggregation number (greater than 1) when the concentrations are within the critical micelle concentration region. When all intermolecular interactions are short ranged, the system undergoes an ordinary liquid–liquid demixing at low concentrations but does not display conventional micellization thermodynamics. It is concluded that shape fluctuations are of paramount importance to the structural properties of micelles near the most probable aggregation number (greater than 1) for near critical micelle concentrations when the chains are reasonably stiff. It is argued that micellar structural fluctuations are important ingredients in the interpretation of light and neutron scattering experiments on micellar solutions. Observed micelles which were much larger than the most probable size for near critical micelle concentrations adopt roughly cylindrical structures. Results on chain ordering near the micelle surface and on chain conformations are compared to those for simple liquid hydrocarbon droplets.

I. Introduction

In this paper we present and discuss the results of an extensive Monte Carlo study of a simple molecular model for micellar aggregates. Preliminary results which focused exclusively on the micellar structural properties implied by the model have been presented previously.[1] These structural properties are scientifically important and interesting.[2,3] We have now investigated these structural properties for a wide range of interaction potential energy parameters which define the model. However, one goal of this work is a molecular understanding of the forces which cause the assembly of membranes and micelles. Indeed, micellar solutions are often taken as convenient systems in which to study the forces responsible for the structure and thermal stability of molecular biological assemblies.[4] For these purposes, it is essential to carefully study the thermodynamic properties implied by the model, and especially their dependence on the molecular interactions involved. Thus, it is important that we can now accurately calculate the global behavior of the thermodynamic properties which govern the formation of these aggregates.

The molecular model we study has been described previously.[1] In comparison with specific micellar solutions, it is extremely simple. We view it as a generic micelle model and try to draw generally valid qualitative conclusions from it. On the other hand, the model we study is much more detailed than any other molecular models which have been the subject of systematic statistical thermodynamic study so far. The results presented here should facilitate subsequent direct computer simulation of micellar solution models which are more realistic on a molecular level, despite the fact that those larger scale calculations must be expected to be limited in the type of thermodynamic information they can yield.

An example of the kind of generally valid, qualitative conclusions we find is a direct conceptual connection between the spatial extent of the repulsive interactions associated with the head groups and the spatial extent of the largest aggregates formed in appreciable concentrations. If these head-group repulsions are short ranged on a molecular length scale, we do not find typical micellization thermodynamics; especially we do not find a critical micelle concentration feature occurring before a macroscopic liquid–liquid phase *transition* intrudes. Despite the fact that repulsions associated with head groups oppose attractions associated with tail groups, if short-ranged interactions or thermodynamic conditions are adjusted to favor micelle growth at small micelle sizes, then some other additional mechanism operative on a larger length scale is required to terminate cluster growth at large sizes. This suggests that special attention should be given to the *spatial range* at which the repulsive forces saturate. These results lead us to the physically natural conclusion that the spatial range of the repulsive forces must be comparable to the spatial extent of the most typical micellar aggregates just above the critical micelle concentration. This point is basic to understanding whether a particular surfactant under particular thermodynamic conditions will form organized structures of infinite extent such as membranes, or other macroscopic ordered phases. This suggests that the complex thermodynamic behaviors of these systems should be very sensitive to the long-ranged intermolecular interactions. This point of view seems to be implicit in the approach of Wennerstrom and co-workers[2] which treats just the electrostatic interionic forces in theoretically describing the phase behavior of soaps. Note that these conditions are largely independent of detailed alterations of chain packing, such as incremental changes in near-neighbor head-group distances, with increasing micelle size. Instead, *the spatial extent and global shape of the micelles* are especially important.

The thermodynamic results implied by the model are presented in the next section, after we review some relevant features of the model. The micelle structural results are discussed in section III. It may be noted here that roughly cylindrical shapes are adopted by the micellar aggregates which are much larger than the most probable size (greater than 1) in the critical micelle concentration

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[†] Alfred P. Sloan Research Fellow, 1981–3.

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(2) H. Wennerstrom and B. Lindman, *Phys. Rep.*, **52**, 1 (1979).

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